

Magnetic Transitions and Ferromagnetic Clusters in $\text{RuSr}_2(\text{Eu,Ce})_2\text{Cu}_2\text{O}_{10+\delta}$

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Abstract

The macroscopic magnetizations of a $\text{RuSr}_2(\text{Eu}_{0.7}\text{Ce}_{0.3})_2\text{Cu}_2\text{O}_{10+\delta}$ sample were investigated. A ferromagnet-like transition occurs around T_M in the low-field magnetization. Highly nonlinear $M(H)$, non-Curie-Weiss susceptibility, and slow spin-dynamics, however, were observed up to $T_1 \approx 2-3 T_M$. In addition, an antiferromagnet-like differential-susceptibility maximum of Ru appears around a separate temperature T_{AM} between T_1 and T_M . The data are therefore consistent with a phase-separation model: superparamagnetic clusters (or short-range spin-orders) are first precipitated from the paramagnetic matrix below T_1 , followed by an antiferromagnetic transition of the matrix at T_{AM} and an apparent ferromagnetic (FM) transition around T_M , where the long-range spin-order is established in the FM species imbedded in the matrix.

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I. INTRODUCTION

The magnetic structure of the rutheno-cuprates $\text{RuSr}_2\text{RCu}_2\text{O}_{8+\delta}$ (Ru1212R) and $\text{RuSr}_2(\text{R,Ce})_2\text{Cu}_2\text{O}_{10+\delta}$ (Ru1222R), where $\text{R} = \text{Gd}, \text{Eu}, \text{and Y}$, remains a topic of debate even after extensive investigations of their macroscopic magnetization (M), neutron powder diffraction (NPD), and nuclear magnetic resonance (NMR) in the last few years.^{1,2,3,4,5,6} Even in the relatively simple case of Ru1212, a large discrepancy exists. A NPD investigation reported that the Ru-spins ordered antiferromagnetically (AFM) *along* the c -axis with a rather stringent upper limit of 0.1 and 0.2 μ_B/Ru at $H = 0$ and 7 T, respectively, for the ferromagnetic (FM) components of Ru.³ The spontaneous magnetization of ≈ 800 emu/mole at 5 K, however, leads to a significantly higher value of 0.28 μ_B/Ru after a geometric correction-factor of 2 for the random grain-orientation.¹ The difference between the extrapolated zero-field magnetization of 0.7 μ_B/Ru and the NPD estimation of ≈ 0.2 μ_B at 7 T is even larger.^{3,5} The discrepancy is similarly striking when the NMR data are included. The zero-field NMR data suggest that the aligned moment, ≈ 1.6 μ_B/Ru , should be *perpendicular* to the c -axis instead, and that the FM component should be a large part of the moment.⁶ While at least two other NPD studies claim similarly negligible FM components,^{7,8} both the large FM moment and the perpendicular spin-direction were confirmed by independent NMR measurements.⁹ These conflicts will be difficult to reconcile, in our opinion, if these rutheno-cuprates are microscopically homogeneous.

The magnetic behavior of Ru1222 appears to be even more complicated.^{2,4} On one hand, the two compounds share the same basic features: well-defined FM-like features in low-field magnetizations around a transition temperature of T_M ; spontaneous moments far larger than 0.1 μ_B/Ru ;^{1,2,10} similar Curie constants and FM-like Curie-Weiss (C-W) temperatures;^{5,10} and significant nonlinear isothermal $M(H)$ with large extrapolated zero-field moments up to 2–3 T_M .^{2,4,5} In particular, when the zero-field NMR suggests similar large FM components,^{6,11} a preliminary NPD investigation observed a negligible ferromagnetic moment in Ru1222Gd as well.¹² The two compounds seem to share an unusual magnetic ground state, which appears AFM-like in the NPD data but FM-like in the $M(H)$ and NMR signals. On the other hand, quantitative differences exist between them: both the nonlinearity in $M(H)$ and the spontaneous magnetization are significantly larger in Ru1222.^{2,10}

It is interesting to note that some of the features seem to be characteristic of magnetic nanoparticles (superparamagnets). As will be discussed below, the nonlinear $M(H)$ far above T_M and the discrepancy between the NPD and NMR data are very reminiscent of some manganites, where phase-separations and the formation of ferromagnetic nanoclusters are well documented. A close re-examination of the magnetic properties of rutheno-cuprates, therefore, may help to resolve the magnetic structure of Ru1222. Indeed, our static and dynamic magnetic data of a Ru1222Eu sample with $T_M \approx 65$ K are consistent with a phase-separation model: ferromagnetic clusters (or short-range spin-orders) are first precipitated from the paramagnetic matrix below $T_1 \approx 160$ –180 K, followed by an AFM transition of the matrix around $T_{AM} \approx 104$ K and an apparent FM transition around T_M , which we attribute to the establishment of long-range FM spin-orders. The model offers a possible explanation for the conflicting NPD/NMR data as well as the Josephson-junction-like superconductivity at lower temperatures,^{3,6,13} although detailed structure investigations are needed.

II. EXPERIMENT

Ceramic $\text{RuSr}_2(\text{Eu}_{1-x}\text{Ce}_x)_2\text{Cu}_2\text{O}_{10+\delta}$ samples with $0.3 \leq x \leq 0.5$ were synthesized following the standard solid-state-reaction procedure. Precursors were first prepared by calcining commercial oxides at 400–900 °C under flowing O_2 . Mixed powder with a proper cation-ratio was then pressed into pellets and sintered at 900 °C in air for 24 h. The final heat treatment of the ceramics was done at 1090 °C for 60 h after repeatedly sintering at 1000 °C and regrinding at room temperature.⁴ The structure of the samples was determined by powder X-ray diffraction (XRD) using a Rigaku DMAX-IIIB diffractometer. The XRD pattern of the samples is similar to that previously reported.¹³ There are no noticeable impurity lines in the X-ray diffraction pattern within our experimental resolution of a few percent. The grain sizes ($\approx 2\text{--}20\ \mu\text{m}$) of the ceramic samples were measured using a JEOL JSM 6400 scanning electron microscope (SEM). The magnetizations were measured using a Quantum Design SQUID magnetometer with an *ac* attachment. Only the data of a $\text{RuSr}_2(\text{Eu}_{0.7}\text{Ce}_{0.3})_2\text{Cu}_2\text{O}_{10+\delta}$ sample will be presented here since the features concerned are rather similar in more than five samples with various Ce-doping of $0.3 \leq x \leq 0.5$.

III. DATA AND DISCUSSION

A. *dc* Magnetization and its *H*-Dependence

The zero-field-cooled magnetization, M_{ZFC} , and the field-cooled magnetization, M_{FC} , of the $\text{Ru}_{1222}\text{Eu}$ sample at 10 Oe are shown in Fig. 1. Both M_{ZFC} and M_{FC} rise FM-like with cooling and the separation between M_{FC} and M_{ZFC} develops below 60 K, phenomena similar to those reported previously.^{2,10} Such behavior is typical of magnets with domain-wall pinning. The inflection point of the $M_{FC}(10\text{ Oe})$ is taken as the magnetic transition temperature $T_M \approx 65\text{ K}$ (shown by the arrow in Fig. 1). To consider the effects of possible spin fluctuations, the observed M_{FC}/H at various H is plotted against $t = T/T_M - 1$ since the spin fluctuations in a second-order transition are expected to be universal functions of t after a proper H scaling (Fig. 2).¹⁴ Two features are readily noticed. First, two additional transitions, which are too small to be noticed in the linear M -scale of Fig. 1, appear far above T_M when $H \ll 0.1\text{ T}$. Similar features have been reported before, and attributed to either chemical inhomogeneity or a possible phase separation.^{2,4} Their direct effect on the high-field magnetization, however, seems to be small, *i.e.* both M_{FC} and dM_{FC}/dT appear to be smooth functions of T with no transition-like features at the corresponding temperatures. We will therefore not discuss them further. Second, strong nonlinearity, *i.e.* an H -dependence of M_{FC}/H , appears up to $T_1 \approx 160\text{--}180\text{ K}$ with H between 0.1 and 5 T, where the contributions of the two additional transitions should be negligible. Similar nonlinearity has been noticed previously in both Ru_{1212} and Ru_{1222} up to $t = 1\text{--}2$ and has been attributed to spin-fluctuation,¹⁰ magnetic anisotropy,⁵ and rotation of the canting angle.² It should be noted that the magnetic hysteresis is rather small above T_M . The separation between the H -increase and the H -decrease branches in a $\pm 5\text{ T}$ M - H loop is less than 1% with $T > 70\text{ K}$ and $H \geq 500\text{ Oe}$. The M_{FC} presented here, therefore, can be treated as the equilibrium magnetization and discussed in terms of the free energy involved.

Although H -dependent $M(H)$'s are a common phenomena in magnets near their transition temperatures due to fluctuation, its appearance up to $t = 1\text{--}2$ is highly unusual. In principle, the spin fluctuation near T_M is determined by the competition between the magnetic

interaction-energy $M_0 V_c H$ and the thermal energy $k_B T$, where M_0 and V_c are the aligned moment and the coherent volume, respectively. The H -dependence will be significant only if the magnetic energy is comparable to or larger than $k_B T$. The value of $M_0 V_c$ above T_M , however, should decrease rapidly with the increase of t and should approach the moment μ_0 of individual spins outside a narrow critical region based on the scaling theory.¹⁴ Far above T_M , the fluctuation-caused nonlinearity should only exist at $H \geq k_B T / \mu_0$. The layered structure of Ru1222 should not change the conclusion.¹⁵ Although nonlinear $M(H)$'s far above T_M have been observed in some particular quasi-2D ferromagnets (*e.g.* $\text{La}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$), evidence generally points to mesoscopic phase-separations, rather than dimensionality, as the cause.¹⁶

This situation is also unlikely to change with the order of the transition. The nucleation energy needed in a first-order transition should suppress the spin alignment at lower fields and make the χ more H -independent. This has been demonstrated in $\text{La}_{0.67}(\text{Ba}_x\text{Ca}_{1-x})_{0.33}\text{MnO}_3$, which exhibits a magnetic transition evolving from first-order to second-order with increasing x .¹⁷ Indeed, the observed $1/\chi = H/M$ above T_M has a weaker H -dependence at smaller x , *i.e.* those with a first-order transition. With $k_B T_M / \mu_0 \approx 30$ T in Ru1222Eu, therefore, it would be hard to interpret its nonlinear $M(H)$ up to $t = 1$ – 2 as simple spin fluctuations.

B. Superparamagnetic Component and Langevin-Function Fits

An extensive nonlinearity far above T_M (*i.e.* a violation of the scale theory), however, may occur if magnetic clusters (or strong short-range correlations), which are a common phenomena in both manganites and cuprates, form. The above free-energy argument will require only a cluster size (or the rigid spin-spin correlation-range) of $k_B T / H M_0$ to create a significant nonlinearity. For example, the nonlinear $M(H)$ in $\text{La}_{1.2}\text{Sr}_{1.8}\text{Mn}_2\text{O}_7$ (a quasi-2D ferromagnet with a $T_M \approx 126$ K) up to $t \approx 0.27$ (160 K) was suggested by Chauvet *et al.* to be related to the 7–9 Å clusters observed by NPD and ESR.^{16,18} In the case of Ru1222, the magnetic size of the possible clusters should be $\geq 50 \mu_B$ around $2 T_M \approx 130$ K to make a significant nonlinearity below 5 T. Such clusters will contain at least 20 Ru ions, based on the estimated moment $\mu_0 \leq 3 \mu_B/\text{Ru}$, and should be regarded as superparamagnets. Experimentally, this suggestion, *i.e.* part of Ru1222 is in a spin-ordered state far above T_M , is also in agreement with the Mössbauer data of Ru1222Gd, where an ordered state with a hyperfine field ≈ 30 T has been demonstrated up to $T_1 \approx 180$ K.²

To make this argument more quantitative, the isothermal M - H of the sample is analyzed using the Langevin function $\text{ctnh}(\mu H / k_B T) - k_B T / \mu H$ of superparamagnetic particles, where μ is the magnetic moment of the particles. This procedure essentially replaces the spin-correlation function of $\Phi(r_i, s_i, r_j, s_j)$ by a step function of $|r_i - r_j|$: the spins are assumed to be tightly aligned within a coherence volume but without any directional correlation at larger distances, where r_i and s_i are the position and the spin-orientation, respectively, of the i th spin. The short-range correlations, therefore, are absorbed into the apparent cluster moment μ and the weaker long-range part is ignored. The function has been routinely used in analyzing the particle sizes of granular magnets by fitting the isothermal $M(H)$ as a superposition of weighted Langevin functions. It has been demonstrated in such cases that the deduced μ is a good approximation of the cluster size if the interparticle interactions are weak, but serves only as a *lower-limit* if the interactions are strong.¹⁹ It has been argued, in fact, that the main effect of interparticle interactions is to raise the effective temperature,

T^* , leading to an underestimation of μ by a factor of T/T^* .¹⁹ The situation is expected to be more complicated near T_M of a second-order transition, where the interactions should be a continuing function of $|r_i - r_j|$, and the spin alignment should be described by the scaling models instead. Experimentally, however, the $M(350\text{ K})$ of $\text{La}_{0.67}\text{Pb}_{0.33}\text{MnO}_3$, a manganite with a second-order transition at $T_M = 336\text{ K}$, still fits remarkably well with the function without additional modifications, *i.e.* either a distribution of μ or an additional linear term on H (Fig. 3a).²⁰ The deduced cluster size, *i.e.* $\approx 2a$ at $t = 1.05$, seems to also be reasonable, at least as a lower limit, where $a \approx 4\text{ \AA}$ is the distance between adjacent Mn-spins. The Langevin function, therefore, seems to be a good phenomenological tool when $t \geq 1.04$, keeping in mind that the μ deduced is only a lower limit. In the case of a first-order transition, larger deviations are expected due to the suppression of M at low fields. As an example, the M of a $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ ceramic sample, which has a first-order transition at 265 K ,²¹ was measured at 275 K ($t = 1.04$). The S -shape M - H , which is the result of domain nucleation,¹⁷ makes the Langevin function a less effective description (Fig. 3b). It is interesting to note, however, that the $\mu \approx 200\text{ }\mu_B/\text{cluster}$ so-deduced is still comparable or smaller than the 15 \AA spin-spin coherence length, *i.e.* $100\text{ Mn}/\text{cluster}$, observed by small-angle-neutron-scattering.²¹ This demonstrates, therefore, that the Langevin function should be proper for a qualitative estimation of the cluster size in Ru1222Eu , at least as its lower limit.

The average M between the H -increase branch and the H -decrease branch in isothermal M - H loops of the Ru1222Eu sample was then calculated and taken as the equilibrium one. The M of the Ru1222Eu sample at 80 K so-obtained (triangles in Fig. 3c), however, deviated significantly from the simple Langevin function (solid line in Fig. 3c). In particular, the M is a linear function of H above 2 T . This should not be a surprise since the paramagnetic background of Eu is expected to be large in any case, and an additional linear term should be added to the Langevin function. In fact, this is obvious even in the raw data of both Ru1212 and Ru1222 , where the M above $3\text{--}4\text{ T}$ was previously reported being a linear function of H with an almost T -independent slope.^{2,5} Our data, therefore, were fitted as $\chi_0 H + m \cdot [\text{ctnh}(\mu H/k_B T) - k_B T/\mu H]$ (thick dashed lines in Fig. 3c), with an additional fitting parameter of χ_0 . The fitting is rather good over a broad temperature range (Fig. 4). It is interesting to note two unusual characteristics of the deduced parameters (Fig. 5). First, the μ is large and decreases with T rather slowly over a broad range of $T \leq 150\text{ K}$ (the fitting uncertainty makes the situation at higher temperatures less clear), which is very different from the μ of critical fluctuations (as suggested by the Ni data in the same figure).²² The deduced μ of Ru1222Ru , in fact, is several orders of magnitude larger than that of Ni when $T/T_M > 1.1$ (open diamonds in Fig. 5). Such a large μ , *e.g.* $\approx 300\text{ }\mu_B$ at $T/T_M = 2$, is difficult to understand without a cluster formation (or a short-range spin-spin correlation strong enough to prevail against the thermal disturbance $k_B T$), and justified the use of the Langevin function. Second, the deduced m , which is roughly equal to the “extrapolated zero-field moment” in previous reports, varies with T/T_M only gradually, without any sharp transition-like features across T_M (inset, Fig. 5). For instance, although the major increase of m occurs around $100\text{--}120\text{ K}$, its long tail extends up to $T_1 \approx 160\text{--}180\text{ K}$. It should also be pointed out that the m deduced does not saturate with cooling down to 10 K and is far smaller than the aligned moment of $1\text{--}2\text{ }\mu_B/\text{Ru}$ ($50\text{--}100\text{ emu}/\text{cm}^3$) measured by NMR. This small and T -dependent m (*i.e.* the superparamagnetic component) suggests either a canted AFM ground state or a phase-separation, *i.e.* only a fraction of Ru -spins are gradually FM-aligned. Butera *et al.*, however, have pointed out that the large canting angle, $\approx 20^\circ$

in our case, required would be rather unusual.⁵ The simplest scenario, therefore, would be an eventual precipitation of FM clusters from the paramagnetic matrix. Both the unusual nonlinear $M(H)$ far above T_M and the relatively small m can be self-consistently interpreted in this simple model.

C. Slow Dynamics Far Above T_M

The formation of clusters (or strong short-range spin-spin correlations) can be verified by the dynamic response of the sample. A slow dynamics should be characteristic of a magnetic system with energy barriers comparable to the thermal energy $k_B T$. The energy barrier $(K \cos^2 \theta - M_0 H \cos \theta) V_c$,²³ which can be reduced to $\approx K \cos^2 \theta V_c$ at low fields $H \ll K/M_0$, is much smaller than $k_B T$ in the case of paramagnets, but much larger in typical crystalline ferromagnets, where K and θ are the anisotropy coefficient and the angle between H and the easy axis, respectively. In either case, the magnetic response to the changes of H and T will be either too fast or too slow to be observed in the experimental time-window. An observable slow dynamics, *i.e.* a time-dependent response between 10 and 10^6 s, implies energy barriers of 20–40 times $k_B T$. In a system of isolated magnetic clusters, this corresponds to the existence of clusters with a V_c on the order of 10^{-18} – 10^{-21} cm³ (10–100 Å in diameter) with 10^4 erg/cm³ $< K < 10^7$ erg/cm³ (values typical for ferromagnets). The dynamic magnetization of the Ru1222Eu, therefore, was measured above T_M to verify the formation of clusters. First, the sample was cooled to a temperature between 60 and 100 K at zero field. A field of $H = 5$ Oe was added after the temperature was stabilized for 30 min. The dc M_{ZFC} was then continuously measured as a function of time t_1 , where t_1 is the time after the field is activated (Fig. 6a). A significant logarithmic increase of the magnetization with time exists over a broad temperature range. In particular, the rate $d \ln M / d \ln t_1$ is far larger than our experimental uncertainty of ≈ 0.003 below 90 K. A logarithmic relaxation, in principle, may occur if either the related energy barrier $K \cos^2 \theta V_c$ has a particular distribution or a strong interparticle interaction exists.^{23,24} In both cases, however, the effective barrier (at least its lower limit) is $k_B T [(d \ln M / d \ln t_1)^{-1} + \ln(t_1/\tau)] \approx k_B T (d \ln M / d \ln t_1)^{-1} = 7.4 \cdot 10^{-20}$ J at 80 K, where τ is a characteristic time typically $\approx 10^{-10}$ s. The $V_c \approx 7.4 \cdot 10^{-20} / \mu_B H_{ai}$ (in units of the FM moment involved), therefore, will be 700 μ_B with an estimated anisotropy field H_{ai} of 11 T, *i.e.* the anisotropy field observed in Ru1212Gd along c .⁵ It is interesting to note that the estimated value is in rough agreement with the size of $10^3 \mu_B$ from the Langevin-function fit at the same temperature. Second, the sample was cooled at an $H = 0.08$ Oe (the field inhomogeneity is ± 0.01 Oe over the scanning length of 4 cm) from 200 K to a designated temperature between 70 and 90 K with different cooling rates between 0.1 and ≈ 50 K/min (by mechanically dropping the sample into a precooled chamber). The M_{FC} under such conditions was then measured at 30-min intervals after the temperature was stabilized. The decrease of M_{FC} with the cooling rate at temperatures far above T_M , a slow spin-alignment during the cooling, is again observed (Fig. 6b).

It should be pointed out that the above temperature range is where two additional transitions appear, and that part of the relaxation may be associated with the corresponding species. However, the large $d \ln M / d \ln t_1$, as well as its smooth T -dependence below T_M , where the additional species should be negligible, suggests that there should be a significant superparamagnetic component for the 65-K species as well. This is also supported by the slow ac dynamics in Ru1222Eu reported previously.²⁵

D. Non-Curie-Weiss Susceptibility and the Separated AFM Transition

It should be noted that the linear term χ_0 so-deduced from the Langevin-function fit, which should be roughly equal to the differential susceptibility at 5 T in our case, offers another opportunity to verify the possible phase separations, *i.e.* a spatially separated matrix, from the clusters embedded. The deduced χ_0 is displayed in Fig. 7 as a function of temperature. To subtract the contributions of Eu, Ce, and CuO_2 , we follow the procedure proposed by Butera *et al.* for Ru1212Eu and adopted by Williams *et al.* for Ru1222Eu , *i.e.* using the Van Vleck susceptibility of Eu^{3+} and a T -independent term of $8 \cdot 10^{-6}$ for CuO_2 , and ignoring the contribution of Ce.^{5,10} It should be pointed out that the Eu/Ce contributions are less certain in the case of Ru1222 . For verification, the same procedure was used for a comparison with the measured χ in the nonmagnetic $\text{NbSr}_2\text{Eu}_{1.4}\text{Ce}_{0.6}\text{Cu}_2\text{O}_{10-\delta}$ (Nb1222Eu), which has the same $(\text{Eu}_{0.7}\text{Ce}_{0.3})_2\text{O}_2$ block (inset, Fig. 7). The good agreement demonstrates that the procedure is valid and that the contribution of Ce is small. In any case, this Eu/Ce/ CuO_2 contribution is relatively small ($\approx 1/2$ of the χ_0 observed) and likely to vary with T only monotonically (Fig. 7). The Ru seems to be a major contributor to the χ_0 (a similar conclusion has been reached previously^{5,10}). This suggestion is supported by the facts that the raw χ_0 of Ru1222Eu exhibits a T -dependence very different from that of $\text{NbSr}_2\text{Eu}_{1.4}\text{Ce}_{0.6}\text{Cu}_2\text{O}_{10-\delta}$ and the Ru contribution to the Curie constant, $\approx 2.6 \mu_B/\text{Ru}$ after this background-subtraction procedure, seems to be reasonable. A large amount of paramagnetic Ru-spins, therefore, should coexist with the ferromagnetic clusters in the sample over a broad temperature range. A likely scenario, therefore, appears to be a phase separation between the FM clusters and a paramagnetic matrix, although alternate interpretations, *i.e.* peculiar spin canting or magnetic anisotropy, should also be considered (see discussions below).

To further verify the phase-separation proposed, *dc* and differential *ac* susceptibilities up to 400 K were measured and analyzed. Above $T_1 \approx 180$ K, no H -dependence of χ can be noticed; the $M_{FC}(1 \text{ T})/H$ and the $M_{FC}(5 \text{ T})/H$ merge there (Fig. 2). Ru1222Eu , or at least its dominant part, should be in a simple paramagnetic state above T_1 . The C-W law of $\chi = C/(T - T_{CW})$ was then used to fit the data after both the Eu-contribution and a T -independent term of $8 \cdot 10^{-6}$ were subtracted from the raw data. The $1/\chi = H/M_{FC}(5 \text{ T})$ observed between $T_1 \approx 200$ K and 400 K is a linear function of T within our experimental uncertainty of 0.1–1% (inset, Fig. 8). The deduced Ru moment of $2.61 \mu_B$ is in good agreement with that of $\text{RuSr}_2\text{EuCeCu}_2\text{O}_{10-\delta}$ previously reported.¹⁰ The Curie temperature $T_{CW} \approx 80$ K is only slightly higher than the T_M defined from the low- H M_{FC} (Figs. 1,8). Below 180 K, however, the $H/M_{FC}(1 \text{ T})$ is significantly lower than the $1/\chi$ expected from the C-W fit, but the differential susceptibility at 5 T is much higher. Such deviation at so high a t is rather unusual. Theoretically, it has been suggested that the C-W law should be applicable down to the critical region if the spin interactions have an infinite range.²⁶ Even in the case of short-range 3D Ising or Heisenberg interactions, the agreement is typically good down to $t \approx 10^{-1}$.^{22,26} The corrections expected are at a high power of T_M/T , and are typically only 10% or less when $t > 0.3$. Experimentally, the C-W fit of Ni is consistent with the data down to $t \approx 1.1$.²² Although similar deviations have been reported in both spin-glass and manganites, they were attributed to cluster formations and/or phase separations.^{21,27} This can be easily understood. On one hand, the cluster formation and phase separation offer a natural interpretation: the FM clusters will enhance the susceptibility at low fields but suppress the differential susceptibility at high fields due to the depletion of the available

paramagnetic spins. On the other hand, a mean-field treatment leads to a weighted apparent moment of $\mu = (3k_B/N)^{1/2}/[\frac{d}{dT}(1/\chi)]^{1/2}$.²⁷ The gradual increase (decrease) of $\frac{d}{dT}(1/\chi)$ with cooling, therefore, suggests an increase of μ at low field (high field), *i.e.* cluster formation and phase separation. A χ -deviation from the C-W behavior in $\text{La}_{2/3}\text{Ca}_{1/3}\text{MnO}_3$ up to $2 T_M$, for example, has been taken as evidence for the formation of FM-aligned clusters.²¹ The χ of $\text{La}_{1.35}\text{Sr}_{1.65}\text{Mn}_2\text{O}_7$ is even more closely reminiscent of the data in Fig. 8.¹⁶ It is H -independent and follows the C-W law above 380 K with a deduced $T_{CW} \approx 280$ K. Between 280 and 380 K, however, the $H/M(0.5 \text{ T})$ is far below the C-W fit, but the $H/M(5 \text{ T})$ is far above it. Both NPD and ESR further demonstrate that these deviations are the result of phase separations.¹⁶ The similar χ -behavior of Ru1222Eu, therefore, would suggest phase separation and the formation of FM clusters. It is interesting to further note that the “missing” differential susceptibility $\Delta\chi_{0,Ru}$ of $C/(T-T_{CW}) - \chi_{0,Ru} \approx 5 \cdot 10^{-5}$ at 120 K is about 30% of the expected $C/(T-T_{CW}) = 1.65 \cdot 10^{-4}$ (Fig. 8), which is only slightly larger than the ratio of $m(120 \text{ K})/m(10 \text{ K}) \approx 20\%$ (inset, Fig. 5). This is in agreement with the proposed model in which the homogenous paramagnetic Ru1222 above T_1 eventually separates into FM clusters and a matrix on cooling. We further attribute the slight difference between these two ratios to local AFM correlations developed in the matrix. The nonlinear isothermal $M(H)$ and the non-C-W susceptibility up to $2\text{--}3 T_M$, therefore, can be consistently understood. Both are similar to the data observed in manganites and can be self-consistently interpreted as the results of the FM clusters resulting from the possible phase separations.

An AFM-like minimum appears around 120 K in the $1/\chi_{0,Ru}$ of the sample (Fig. 8). AFM correlations seem to develop quickly below this temperature. For example, the $\chi_{0,Ru}$ is only 10% or less of that expected from the C-W fit below 90 K. It should be pointed out that the m at 90 K, *i.e.* the total spins involved in the formation of the FM-like clusters, remains far smaller than the $m(10 \text{ K})$ of 17 emu/cm³. The suppression of $\chi_{0,Ru}$, therefore, should come mainly from the AFM correlations of the matrix. Fisher has proposed, on rather general grounds, that the magnetic specific heat is proportional to $\partial(T\chi)/\partial T$, and that the Néel temperature corresponds to the inflection point $\partial^2(T\chi)/\partial T^2 = 0$ in simple antiferromagnets.²⁸ A numerical differential, therefore, was carried out. The transition temperature $T_{AM} \approx 104$ K so-deduced is almost double the $T_{FM} \approx 65$ K observed (the arrow in Fig. 8). It is interesting to note that the T_{AM} differs from the 120-K dip by only 13%, characteristic of 3D spin ordering.²⁹ It should also be pointed out that the large separation between the T_M and the T_{AM} is not typical of the behavior of homogeneous canted AFM magnets. For example, the M_{FC} onset and the peak of the differential susceptibility in CsCoCl_3 , a 1D Heisenberg canted antiferromagnet, occur at the same temperature, 3.4 ± 0.2 K, within the experimental resolution.³⁰ Ru1222Eu, therefore, is unlikely to be a simple canted AFM magnet with a single transition at T_M . Either several sequential magnetic transitions or a phase separation should have taken place.

At lower temperatures, an FM-like transition occurs around T_M at low fields (Fig. 1). It is a puzzle, however, that there are no anomalies in either m or χ_0 around this temperature, as pointed out previously.⁴ To explore the nature of the T_M transition, the remnant moment was measured in a M - H loop of ± 500 Oe (Fig. 9). It is interesting to note that there is neither a remnant moment nor a significant hysteresis above T_M , although a noticeable m appears there already—a scenario reminiscent of superparamagnets above their blocking temperature. This is in agreement with the cluster size deduced in Fig. 5. Below T_M , however, the remnant moment appears, and the M_{FC} at 100 Oe becomes comparable to the m deduced (Figs. 3,5,9). A significant part of the FM component should possess a magnetic

energy $HM_0V_c \geq k_B T$ below T_M , although a superparamagnetic component may still exist, as suggested by the slow dynamics. A long-range spin-order, therefore, is established at T_M due either to a rapid growth of the cluster size or to a phase-coherent transition among adjacent clusters.

The proposed model, in our opinion, can also offer possible explanations for many conflicting and confusing data previously reported. The conflict between the NPD and NMR data for the magnetic structure, for example, may be attributed to the fact that the two probes have different sensitivities to various magnetic species. The NPD, on one hand, is insensitive to the minor FM nanoclusters due to both the volume fraction, estimated to be $\approx 10\%$ for Ru1212Gd, and the submicron size of the clusters. The sensitivity of NMR (as a *rf* transverse susceptibility), on the other hand, is small for AFM (inversely proportional to the exchange field), large for a single-domain FM (inversely proportional to the anisotropy field), and even larger for FM domain-walls (proportional to the wall mobility). The NMR data of Ru1212/Ru1222, therefore, may be dominated by the minor FM part due to, for example, the small in-plane anisotropy field of ≈ 200 Oe observed.⁵ In fact, a similar (though not as dramatic) situation has been reported in $\text{La}_{0.35}\text{Ca}_{0.65}\text{MnO}_3$. When the zero-field NMR signal of the compound is dominated by the minor FM species with a volume fraction of $\approx 8\%$,³¹ its NPD data show a homogeneous AFM structure.³² The different spin orientations assigned by NPD (*i.e.*, along the *c*-axis) and by NMR (*i.e.*, perpendicular to the *c*-axis) can be naturally understood as well. Similarly, the suppression of the superconducting order parameters inside the FM nanoclusters and the possible tunneling across them again offer a natural mechanism for the granular superconductivity observed.¹³

Two alternate interpretations have been proposed.^{2,5} It has been suggested that either Ru1222 is already in a homogeneous canted AFM state below T_1 (a multi-transition model) or that the FM components along the *c*- and the *ab*-axes depend on H very differently (a two-stage spin-alignment model). In such models, however, several features are expected. a) An anomaly of $\chi_{0,Ru}$ as well as an m jump are expected around T_1 , where a bulk transition occurs. In fact, the $\chi_{0,Ru}$ is determined by the C-W law above T_1 , but by the magnetic anisotropy and/or the cant angle below T_1 in such models. Similarly, m should be zero above T_1 but should be determined by the canted angle, θ , below T_1 . These two totally different mechanisms make the smooth crossovers around T_1 purely coincidental. Experimentally, no discontinuity or anomaly has ever been reported around T_1 , although both T_1 and T_{CW} can be tuned significantly through doping and oxidation.^{2,4} b) The m and the $\chi_{0,Ru}$ should be related between T_1 and T_M through θ and/or the magnetic anisotropy. Their very different T -dependences in Figs. 5 and 8, therefore, will require rather peculiar temperature dependences of the θ and/or the magnetic anisotropy. c) The FM-like transition at T_M as well as the AFM-like one at T_{AM} will be “extra” features in such models.

The situation in Ru1212Eu is slightly different. However, we believe that similar arguments apply.

IV. SUMMARY

Nonlinear $M(H)$, non-C-W behavior, and slow spin dynamics have been observed in a Ru1222Eu sample between $T_M = 65$ K and $T_1 = 180$ K, suggesting the formation of superparamagnetic clusters 10^2 – $10^3 \mu_B$ in size. Additionally, the differential susceptibility $\chi_{0,Ru}$ shows an AFM transition at $T_{AM} \approx 104$ K. We therefore propose a phase-separation model: the sample is a mesoscopic mixture of FM clusters and a paramagnetic matrix

between T_1 and T_M , followed by an AFM transition of the matrix at T_{AM} and a long-range phase-coherent transition in the imbedded clusters at T_M . This model offers a possible interpretation for many conflicting data, but it needs to be verified by further structure investigations.

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 - ¹⁵ In a second-order transition, it is widely accepted that the scaling equation can be written in a dimensionless form of $(HM_0/MH_0)^{1/\gamma} = t + (M/M_0)^{1/\beta}$, where γ , β , $M_0 = N_a\mu_0$, $H_0 = k_B T_M/\mu_0$, and N_a are two critical exponents, two critical amplitudes, and the Avogadro's number, respectively.¹⁴ The scaled susceptibility (MH_0/HM_0) , therefore, is $t^{-\gamma}[1 + (H/H_0)^{1/\beta}/(t-1)^{1+\gamma/\beta}]^{-\gamma} \approx t^{-\gamma}\{1 - \gamma[(H/H_0)/t^{\beta+\gamma}]^{1/\beta}\}$ to the lowest order of H/H_0 . The H -dependence, therefore, can only be observed at an H comparable to $H_0\gamma^{-\beta}t^{\beta+\gamma}$, and should

be rapidly suppressed with temperature as $1/t^{1+\gamma/\beta}$. Although the critical exponents depend on the dimensionality, the predicated $1 + \gamma/\beta$ is 3 in the mean field theory and 5.3 in the 3D Heisenberg model, but 15 in the 2D Ising model.¹⁴ Experimentally, the values of $1 + \gamma/\beta$ range from 3 (some 3D magnets) to > 10 (quasi-2D magnets) [Z. Q. Qiu, J. Pearson and S. D. Bader, Phys. Rev. Lett. 67, 1646 (1991)].¹⁴ The value of $1 + \gamma/\beta$ is even larger in 2D magnets. When the stronger fluctuation in quasi-2D magnets severely suppresses the spin alignments below T_M , therefore, it makes the $M(H)$ even more linear above T_M .

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FIG. 1: M/H of the $\text{RuSr}_2(\text{Eu}_{0.7}\text{Ce}_{0.3})_2\text{Cu}_2\text{O}_{10+\delta}$ sample at 10 Oe. \bullet : ZFC; \circ : FC. The arrow indicates the inflection point T_M of the $M_{FC}(T)$.

FIG. 2: $\chi = M_{FC}/H$ of several compounds. Solid symbols: Ru1222Eu with $H = 0.0005, 0.01, 0.1, 1, 2$, and 5 T from top to bottom.

FIG. 3: M vs H for: a) $\text{La}_{0.67}\text{Pb}_{0.33}\text{MnO}_3$ at 350 K ($t = 1.05$); b) $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ at 275 K ($t = 1.04$); and c) Ru1222Eu at 80 K ($t = 1.27$). Symbols: data; —: fit to the Langevin function; - - -: fit to the Langevin function with an additional linear term.

FIG. 4: M vs H for Ru1222Eu at 70, 80, 90, 100, 110, 120, and 130 K from top to bottom. Symbols: data; —: fit to the Langevin function with a linear term (see text).

FIG. 5: The estimated cluster size in the Ru1222Eu sample (\bullet) and in Ni (\diamond).²² Inset: the saturation moment m of the proposed magnetic species in Ru1222Eu.

FIG. 6: a) The relaxation of the M_{ZFC} at 5 Oe. b) The M_{FC} at 0.08 Oe with different cooling rates. Measurements were done at the temperatures marked on the right side.

FIG. 7: The extracted linear term χ_0 (\bullet) of Ru1222Eu and the estimated contribution from Eu^{3+} and CuO_2 (—). Inset: —: the estimated contribution from Eu^{3+} and CuO_2 to $\text{NbSr}_2\text{Eu}_{1.4}\text{Ce}_{0.6}\text{Cu}_2\text{O}_{10+\delta}$; \bullet : data (courtesy of I. Felner).

FIG. 8: The T -dependence of $1/\chi$ due to Ru in Ru1222Eu. \triangle : $H/M_{FC}(1 \text{ T})$; ∇ : $H/M_{FC}(5 \text{ T})$; \square : differential susceptibility at 5 T; —: the Curie-Weiss fit. Inset: $1/\chi$ between 200 and 400 K. \bullet : data; —: the C-W fit.

FIG. 9: The remnant magnetization of Ru1222Eu after a ± 500 Oe field cycle at various temperatures.

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